

The Stability Constants for Complexes between Oxovanadium(IV) and Squaric Acid

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The formation of complexes between the oxovanadium(IV) ion and squaric acid has been studied at 25°C with spectrophotometric methods in solutions in which the total molarity was held constant at 3 M by the addition of NaClO₄. The total concentrations of oxovanadium(IV) perchlorate and sodium squarate ranged from 5 to 100 mM and 0.1 to 2 mM, respectively. The pH range was 1.6–2.8. Preliminary constants were obtained graphically. These were then refined with Sillén's generalized least squares program "Letagrop". The experimental data could best be explained in terms of the following equilibrium in the VO²⁺–H⁺–C₄O₄²⁻ system:



The error given corresponds to 3σ in β, where σ is the standard deviation in β.

In connection with studies on complex formation between the squarate ion, C₄O₄²⁻, denoted A²⁻ in the following, and transition metal ions, we have found that nickel(II) forms very weak complexes.¹ According to Tedesco and Walton,² however, complexes with metal ions of higher valency [iron(III), aluminium(III), and uranium(VI)] are stronger. As a complement to our investigation on complex formation with nickel(II) with 8 *d*-electrons we have now chosen vanadium(IV) with 1 *d*-electron.

EXPERIMENTAL

Chemicals and analyses. Oxovanadium(IV) perchlorate was prepared from vanadium(IV) oxide (Schuchardt) by dissolving in an excess of 6 M perchloric acid (Merck *p.a.*). The solution was neutralized by adding a solution of sodium hydroxide (Bohus EKA *p.a.*). Oxovanadium hydroxide was then precipitated by the dropwise

addition of the sodium hydroxide solution as long as any precipitate was formed. The precipitate was centrifuged, washed and dissolved in a slight excess of perchloric acid, as described by Rossotti and Rossotti.³ The concentration of vanadium(IV) in the solution was determined by titration with a standardized potassium permanganate solution. The solution was also tested for the presence of vanadium(V) in the way described by Rossotti and Rossotti. No traces of vanadium(V) were found. The free hydrogen ion concentration was determined by Gran titrations.⁴

Perchloric acid, sodium perchlorate, and sodium squarate solutions were prepared as described elsewhere.⁵

Apparatus. The *ultra-violet absorption measurements* were performed as described previously.¹ The absorbance was measured at 25 different wavelengths ranging from 240 to 300 nm.

The solutions to be examined were prepared by mixing solutions of oxovanadium(IV) perchlorate, sodium squarate and perchloric acid, the total molarity being held constant at 3 M by the addition of a sodium perchlorate solution. The total concentrations of sodium squarate, *A*, and oxovanadium(IV) perchlorate, *B*, varied within the ranges 0.1–2 mM and 5–100 mM, respectively. The concentration of the free squarate ion, A²⁻, however, ranged from only 0.003 to 0.3 mM, owing to the varying hydrogen ion and VO²⁺ concentrations.

The *free hydrogen ion concentration, h*, was measured in each solution by emf methods, as described previously.⁵

To obtain a reasonable concentration of squarate ions, A²⁻, it is necessary to work at as high a pH as possible (*cf.* Fig. 1). On the other hand, it is desirable to avoid hydrolysis of VO²⁺. The pH range was thus chosen so that the concentrations of the hydrolysis complexes were kept < 10⁻⁵ M, as calculated by means of the formation constants determined by Rossotti and Rossotti.³ The pH range chosen was therefore 1.6 ≤ pH ≤ 2.8.

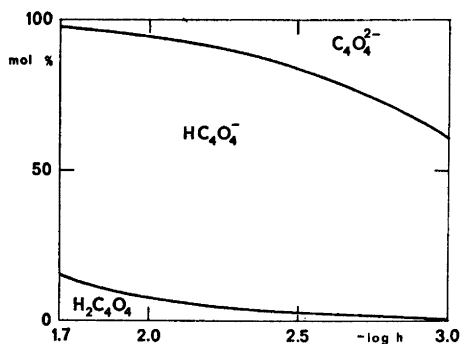


Fig. 1. The distribution of squaric acid species as a function of $-\log h$.

LIST OF SYMBOLS

- A total concentration of squaric acid, H_2A
 a free concentration of squarate ions, A^{2-}
 B total concentration of VO^{2+}
 b free concentration of VO^{2+}
 H total concentration of hydrogen ions, H^+
 h free concentration of hydrogen ions, H^+
 c_{pqr} free concentration of $(VO)_pH_qA_r^{(2p+q-2r)+}$
 β_{pqr} equilibrium constant for the reaction
 $pVO^{2+} + qH^+ + rA^{2-} \rightleftharpoons (VO)_pH_qA_r^{(2p+q-2r)+}$
 defined so that
 $c_{pqr} = \beta_{pqr} b^p h^q a^r$
 ϵ_{pqr} molar absorptivity for the complex
 $(VO)_pH_qA_r^{(2p+q-2r)+}$
 A_s absorbance
 l optical path length
 $s = (A_s - l \epsilon_{100} b) / Al$

MEASUREMENTS

Both the components of the squaric acid system and the VO^{2+} ion show strong absorption in the UV region. For the VO^{2+} ion the absorption increases with decreasing wavelength. In Fig. 2 the experimentally determined absorbances of a solution with $A = 1.000$ mM, $B = 20.00$ mM and $-\log h = 2.58$ are shown, as well as the sum of the calculated absorbances of two solutions with the same A and B values, respectively, and the same h value. There are large differences between the curves and thus VO^{2+} would appear to form squarate complexes.

Of the measurements at 25 different wavelengths those at 16 wavelengths were chosen to determine the stability constants and the molar

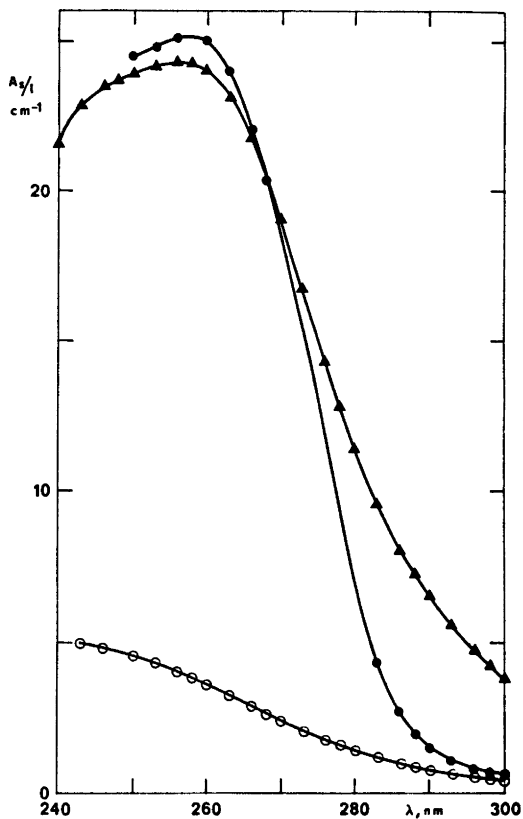


Fig. 2. Experimentally determined absorbances (\blacktriangle) for a solution with $A = 1.000$ mM, $B = 20.00$ mM, and $-\log h = 2.58$, compared with the sum of the calculated absorbances (\bullet) for two solutions with $A = 1.000$ mM, $B = 0$ mM, $-\log h = 2.58$ and $A = 0$ mM, $B = 20.00$ mM, $-\log h = 2.58$, respectively. The calculated absorbances (\circ) for the last solution only are also shown.

absorptivities for the complexes. Eight of these correspond to wavelengths in the range 250–268 nm, where the HA^- and A^{2-} ions show strong absorption and eight correspond to wavelengths in the range 283–300 nm, where the absorption of the VO^{2+} complexes dominate. The other measurements were used only to determine the molar absorptivities at the wavelengths used.

The VO^{2+} squarate solutions were not as stable as those of nickel(II),¹ the absorbances decreasing gradually at all the wavelengths used. The decrease was constant during the 2 months during which the measurements were made and largest in solutions with the highest A and B

values. In all the solutions the decrease was < 0.4 % per day. The pH values were constant or showed a very small decrease. It would seem probable that a redox reaction took place between the VO^{2+} ion and a component of the squaric acid system, and, since $B \gg a$, the decrease in B was negligible. The decrease in absorbance was not affected when a stream of nitrogen gas was passed through the solutions and these were then kept in a nitrogen atmosphere.

In the graphical calculations the first absorbances measured one day after the preparation of the solutions were used, while in the "Letagrop" calculations the measured absorbances were corrected for the estimated decrease.

TREATMENT OF DATA

The absorbance, A_s , at a given wavelength in a solution may be expressed as follows:

$$A_s = l \sum_p \sum_q \sum_r \epsilon_{pqr} c_{pqr} = l \sum_p \sum_q \sum_r \epsilon_{pqr} \beta_{pqr} b^p h^q a^r \quad (1)$$

As is described in the work on nickel(II) squarate complexes,¹ the ϵ_{021} , ϵ_{011} , and ϵ_{001} values were determined by means of the spectrophotometric version of the "Letagrop" program.⁶ The stability constants for squaric acid, obtained from the emf measurements⁵ were used. The ϵ_{100} values were determined in solutions where $A=0$ and $25 \text{ mM} \leq B \leq 100 \text{ mM}$, also using the "Letagrop" program.

Owing to the low total concentration of squaric acid, $A \leq 2 \text{ mM}$, complexes with $r=1$ seem to be the most likely and therefore $q=0$ or 1 are more probable than higher values of q . With ϵ defined as

$$\epsilon = (A_s - l\epsilon_{100}b)/Al$$

eqn. (1) can be transformed to

$$\epsilon = (\epsilon_{001} + \epsilon_{011}\beta_{011}h + \epsilon_{021}\beta_{021}h^2 + \sum_p \epsilon_{p01}\beta_{p01}b^p + \sum_p \epsilon_{p11}\beta_{p11}b^p h) / (1 + \beta_{011}h + \beta_{021}h^2 + \sum_p \beta_{p01}b^p + \sum_p \beta_{p11}b^p h) \quad (2)$$

or

$$\frac{\epsilon(1 + \beta_{011}h + \beta_{021}h^2) - (\epsilon_{001} + \epsilon_{011}\beta_{011}h + \epsilon_{021}\beta_{021}h^2)}{\epsilon b} = \frac{-\sum_p (\beta_{p01} + \beta_{p11}h)b^{p-1} + \frac{1}{\epsilon} \sum_p (\epsilon_{p01}\beta_{p01} + \epsilon_{p11}\beta_{p11}h)b^{p-1}}{\quad} \quad (3)$$

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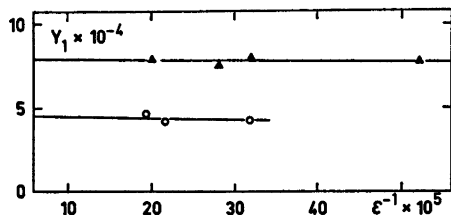


Fig. 3. The left-hand side of eqn. (3) divided by h , Y_1 , as a function of ϵ^{-1} for $\lambda=293 \text{ nm}$, $A=1.000 \text{ mM}$, and varying h values. The following B values were used: \blacktriangle 20.00 mM and \circ 39.30 mM.

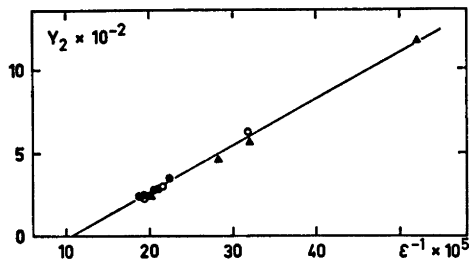


Fig. 4. The left-hand side of eqn. (3), Y_2 , as a function of ϵ^{-1} for $\lambda=293 \text{ nm}$, $A=1.000 \text{ mM}$, and varying h values. The following B values were used: \blacktriangle 20.00 mM, \circ 39.30 mM, and \bullet 100.0 mM. From the slope and intercept $\beta_{101} = 298 \text{ M}^{-1}$ and $\epsilon_{101} = 9440 \text{ M}^{-1} \text{ cm}^{-1}$ were obtained. For solutions with the same A and B values the concentration of free squarate ions, a , decreases with increasing h as does the concentration of the vanadium(IV) complex. The points for solutions with the highest h values (and thus the lowest ϵ values at $\lambda=293 \text{ nm}$) are to be found to the right in the figure.

In solutions where $B \gg A$, b can be replaced by B . To test whether or not VO^{2+} complexes containing hydrogen ions are formed, those with $q=0$ were omitted and all terms in eqn. (3) were divided by a factor h . The left-hand side of the equation was then plotted against ϵ^{-1} (cf. Fig. 3). When data from solutions with $A=1.000 \text{ mM}$, $B=20.00 \text{ mM}$ or 39.30 mM , and varying h values were used, it was possible to draw straight lines through the points. These almost horizontal lines imply that $\sum_p \beta_{p11} B^{p-1} < 0$ and thus that $(\text{VO})_p \text{HA}^{(2p-1)+}$ would not appear to be the main complexes formed.

VO^{2+} complexes with $q=1$ were then omitted in eqn. (3) and the left-hand side was plotted against ϵ^{-1} (cf. Fig. 4). Data from solutions with

$A = 1.000$ mM, $B = 20.00$ mM, and varying h values were used and a linear correlation was obtained. Data from solutions with other B values were then inserted and the new points still indicated the same line. $\sum_p \beta_{p01} B^{p-1}$ and $\sum_p \epsilon_{p01} \beta_{p01} B^{p-1}$ are thus independent of B , *i.e.* $p = 1$. From the slope and intercept of the line the following constants were obtained:

$$\begin{aligned} \beta_{101} &= 298 \text{ M}^{-1} \\ \epsilon_{101} &= 9440 \text{ cm}^{-1} \text{ M}^{-1} \\ \text{for } \lambda &= 293 \text{ nm.} \end{aligned}$$

In order to obtain more accurate results, the data were processed with the spectrophotometric version of the "Letagrop" program.⁶ The refinement of the constant gave the following best value:

$$\begin{aligned} \beta_{101} &= (297 \pm 30) \text{ M}^{-1} \\ \log \beta_{101} &= 2.47 \pm 0.04 \end{aligned}$$

The error squares sum, defined as

$$U = \sum \left(\frac{A_{s,\text{calc}} - A_s}{l} \right)^2$$

was 7.79 for 497 A_s values. Calculations made using "relative errors" and

$$U_r = \sum \left(\frac{A_{s,\text{calc}} - A_s}{A_s} \right)^2$$

yielded the same β_{101} value ($\log \beta_{101} = 2.47 \pm 0.03$) but slightly different standard deviations, *i.e.* smaller in β and larger in ϵ .

Efforts were also made to explain the experimental data by inserting other complexes [*i.e.* (pqr) = (111) or (201), together with (101)] and processing them simultaneously. The improvement in U was, however, small and the standard deviations in β were large. It would therefore seem that no other complexes were present in detectable amounts.

RESULTS AND DISCUSSION

The experimental data could best be explained by the presence of the complex, VOA, with the formation constant

$$\log \beta_{101} = 2.47 \pm 0.04$$

where the error given corresponds to an error of 3σ in β , σ being the standard deviation. This β

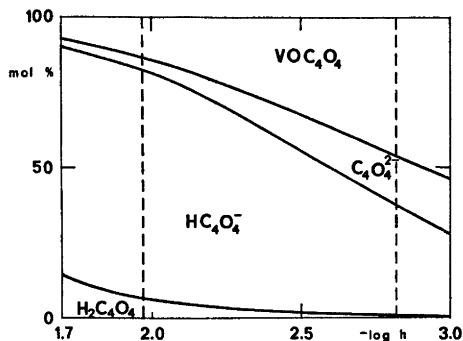


Fig. 5. The distribution of squaric acid species as a function of $-\log h$ for the oxovanadium(IV) squarate system when $B = 10.00$ mM. Only the $-\log h$ values between the dashed lines have been used.

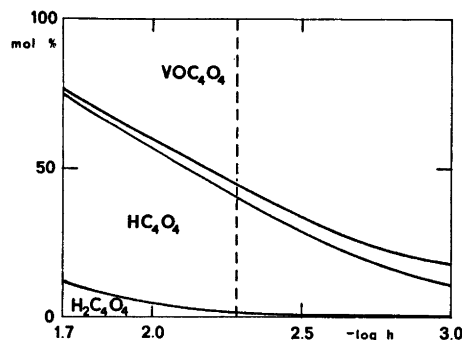


Fig. 6. The distribution of squaric acid species as a function of $-\log h$ for $B = 40.00$ mM. Only the $-\log h$ values to the left of the dashed line have been used.

value has been used, together with the previously determined $\log \beta_{011} = 3.19$ and $\log \beta_{021} = 4.15$, to calculate the distribution of the squarate ion, A^{2-} , between the different complexes for different vanadium concentrations (*cf.* Figs. 1, 5, and 6). Despite the rather low pH and thus the low percentage of free A^{2-} ions, about 50% of the squaric acid can be bound in the form of a vanadium(IV) complex.

The UV spectrum of the VO^{2+} complex differs considerably from that of the squarate ion (*cf.* Fig. 7) in contrast to the spectra of the weaker nickel complexes.¹ Complex formation between a VO^{2+} ion and a squarate ion thus affects the electronic structure of the latter so that the absorption maximum occurs at a lower wave-

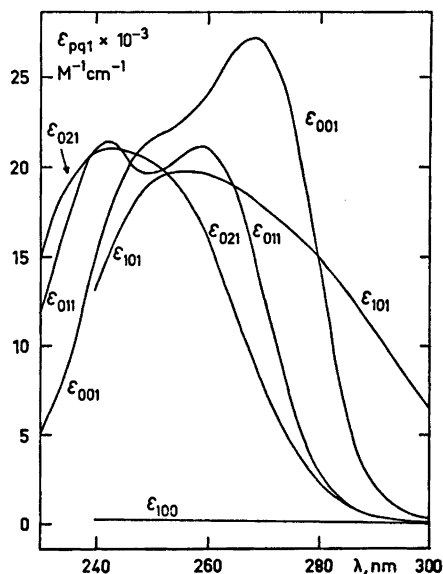


Fig. 7. ϵ_{pq1} as a function of λ . The ϵ_{pq1} values have been calculated by the "Letagrop" program.

length, *i.e.* 256 nm. The molar absorptivities are, moreover, also lower (*cf.* Fig. 7). A similar effect is seen when the squarate ion binds two hydrogen ions. The spectrum of squaric acid shows a maximum at 242 nm and a shape similar to that of the VO^{2+} squarate complex.

The authors would like to thank Professor Georg Lundgren for many stimulating discussions and invaluable help during the preparation of this paper. They are indebted to Mr. Ove Lindgren, *fillic.*, for help with the computer programs and would also like to thank Dr. Susan Jagner for revising the English text of this paper. Financial support from the Swedish Natural Science Research Council is gratefully acknowledged.

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Received December 10, 1973.